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## MEMBRANE SEPARATION TECHNOLOGY IN THE 1980s

Report No. 46-1

Final Report

H. K. Lonsdale

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Bend Research, Inc.  
Bend, Oregon

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## I. INTRODUCTION AND SUMMARY

This report was prepared in fulfillment of Contract No. 956158 between the Jet Propulsion Laboratory and Bend Research, Inc. The purpose of the study was to assess the current status of membrane technology and to identify industrial processes in which membrane technology could effect energy savings or other advantages.

Membrane technology came of age during the 1970s. Aided substantially by several key technical breakthroughs, membrane processes have come to compete favorably with more established technologies in such areas as water desalting, water purification, and gas separations. Several new membrane-based industries have been established, and membrane R&D is now being intensely pursued in the principal industrial countries.

In view of the successes in membrane technology, it is reasonable to ask such questions as "What more can we do with membranes?" and "Can membrane processes effect substantial energy savings in the United States?" This report is intended to be a first step toward answering those questions.

The bulk of the report is concerned with describing the status of membrane technology and the current, promising directions of membrane R&D around the world. We feel that the greatest promise for future applications lies in the extension of current trends, i.e., the development of ultrathin and highly permselective membranes; the use of specific carriers

to enhance permselectivity and, under certain conditions, permit "uphill" diffusion; and the use of new engineering approaches to improve separation efficiency. Membranes may also play an important role in the evolving biotechnology field and in the production of energy from sunlight. We have not attempted to identify the most important separations to which membrane technology should be directed. Rather, we conclude the report by citing where and how to look for opportunities where evolving membrane technology might fit. Specific cases should be the subject of careful economic feasibility assessments.

## II. STATE OF THE ART OF MEMBRANE SEPARATIONS

Membrane separations now form the basis for an international industry with a market estimated to be in excess of \$500 million annually, and growing at a 20-30% compound annual rate. The elements of that industry and our estimates of the respective market sizes are presented below.\*

<u>Industry</u>	<u>Market Size</u> <u>(\$ million/year)</u>
Microfiltration	150
Dialysis, including hemodialysis	200
Electrodialysis	35
Reverse osmosis	100
Ultrafiltration	50
Gas separations, including membrane lungs	15
All others <sup>+</sup>	30

+Includes battery separators, chlor-alkali cells, and fuel cells, for example.

These estimates include membranes, in some cases in module form, and peripheral equipment.

The membrane separations industry was virtually non-existent 30 years ago. The rapid growth was fueled by several key technological developments.

\*This tabulation and certain other information in this report are taken from a review article, "The Growth of Membrane Technology," prepared by the author and scheduled to be published in the Journal of Membrane Science, Volume 10 (1982).



## A. TECHNOLOGY

The important developments in membrane technology occurred in three areas: (1) the membranes themselves, (2) modularization of membranes, and (3) equipment designs that successfully handled concentration polarization. Each of these developments is reviewed briefly below.

### 1. Membranes

Modern membrane separation processes moved ahead rapidly with the discovery of methods for making effectively very thin membranes. This was crucial to the rapid commercialization of reverse osmosis (RO), ultrafiltration (UF), and gas separations, and it was important in microfiltration (MF) as well. These membranes typically have an effective thickness of a micron or less; RO membranes are effectively only 0.1-0.2  $\mu\text{m}$  thick. This leads to very high transmembrane fluxes and consequently low capital costs.

There are five methods that have been examined in detail for making these very thin membranes. These have been reviewed extensively in the literature, and will only be cited here. The methods are the phase-inversion<sup>(1)</sup> or Loeb-Sourirajan<sup>(2)</sup> method; the ultrathin film technique;<sup>(3-5)</sup> dynamic membrane formation;<sup>(6)</sup> plasma polymerization;<sup>(7-8)</sup> and interfacial polymerization.<sup>(9)</sup> Of these, only the first and last are practiced to an appreciable extent today—the others have not been found to be competitive, usually for reasons of nonreproducibility.

Modern membranes are not only very thin, however; they are also highly permselective. That is, they exhibit much higher permeability to certain components in the stream to be processed than to other components. In the language of the industry, they are capable of "clean" separations. There have been only limited applications identified to date of membrane separation processes wherein the separations are not clean. Permselectivity derives from one of two sources. When membranes are used essentially as filters, as in MF and UF, clean separations are achieved by manufacturing the membrane with a well-defined molecular-weight (MW) cutoff, i.e., with a relatively narrow pore-size distribution. In most other cases—i.e., in RO, electro-dialysis (ED), and gas separations—the membranes are essentially nonporous and permselectivity derives from the intrinsic chemical properties of the membrane material. Thus, permselectivity is defined as the permeability ratio:

$$\alpha \equiv \frac{P_1}{P_2}$$

and, because the permeability is the product of a diffusivity and a solubility term,

$$\alpha = \frac{D_1 S_1}{D_2 S_2}$$

in general. Permselectivity thus results from large differences in either the diffusivity or the solubility of the species that permeate the membrane and those that are retained. In some

cases, differences in both D and S are important.

In summary, the membranes in use in most separation processes today, such as cellulose acetate in RO or polysulfone in gas separations, combine two characteristics: thinness and permselectivity. Thinness derives from the fabrication technique, while permselectivity is usually the result of an empirical search through existing polymeric materials.

## 2. Modules

The traditional engineering designs of separation equipment fall into two classes, the plate-and-frame and the tube-in-shell designs. Substantial improvements in each of these designs were fundamental to the success of RO, UF, and gas separations.

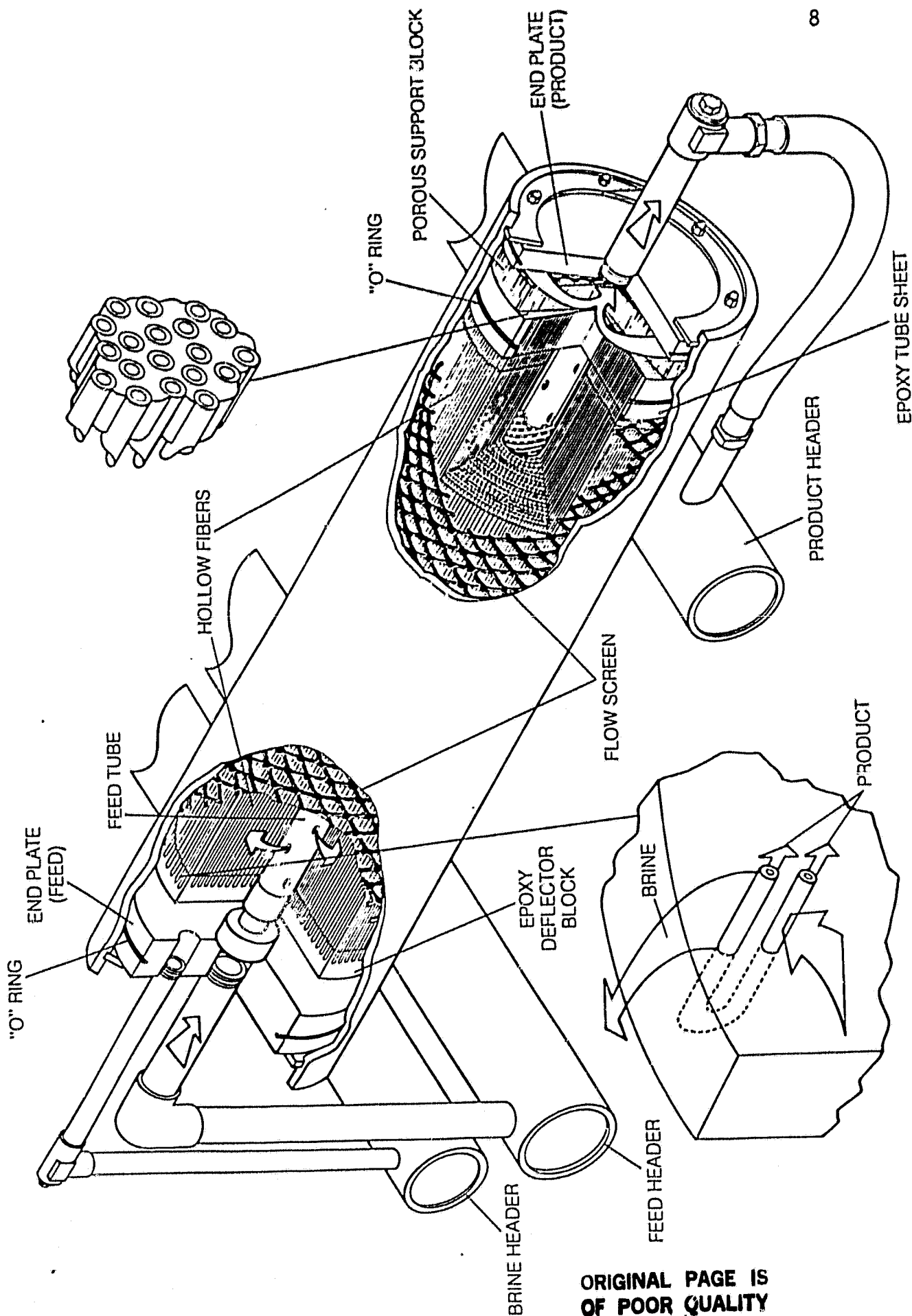
Two types of modules are now in use in each of these three separation applications. The oldest is the so-called hollow-fiber concept, in which many fine, hollow fibers are contained within a pressure vessel. The pressurized feed fluid enters the vessel and permeate is drawn off, usually from the fiber lumens. This is thus a variation on the tube-in-shell design. The second efficient module now in widespread use is the spiral-wound module. In this design, the membrane and spacer materials for the feed and permeate fluids are wound around a perforated tube. The edges of the membrane are sealed to form a kind of envelope, which is sometimes referred to as a membrane leaf. Modern,

large spiral-wound modules are made with multiple leaves in order to shorten the leaf length and thus minimize the pressure drop on the permeate side of the module. Sketches of a hollow-fiber module and a single-leaf spiral-wound module are presented in Figures 1 and 2. Each of these modules has its own characteristic advantage. The hollow-fiber module can be made with extremely high membrane packing density if very fine hollow fibers are used. In the DuPont Permasep<sup>®</sup> RO modules, for example, the packing density is on the order of 3000 ft<sup>2</sup> of membrane per cubic foot of pressure vessel. This results in a very low capital cost for the modularized membrane. The spiral-wound module, because of the need for spacer materials, does not have nearly as high a packing density—about 300 ft<sup>2</sup>/ft<sup>3</sup>—but it is a very convenient way of modularizing membranes that have been cast in flat-sheet form. In fact, the spiral-wound module can be viewed as a plate-and-frame design that has been rolled up. Inexpensive circular pipe can then be used as the pressure vessel. A further advantage of spiral-wound modules is that membrane replacement is very simple.

### 3. Equipment Design

Along with membranes and modules, membrane separation equipment has also evolved in recent years. The principal technical objectives have been to (1) protect the membranes from fouling or chemical attack, (2) minimize the effects of concentration polarization, and (3) provide for cleaning the membranes while they remain in place.

Figure 1. Sketch of a Permasep<sup>®</sup> hollow-fiber reverse-osmosis module, courtesy of DuPont Co.



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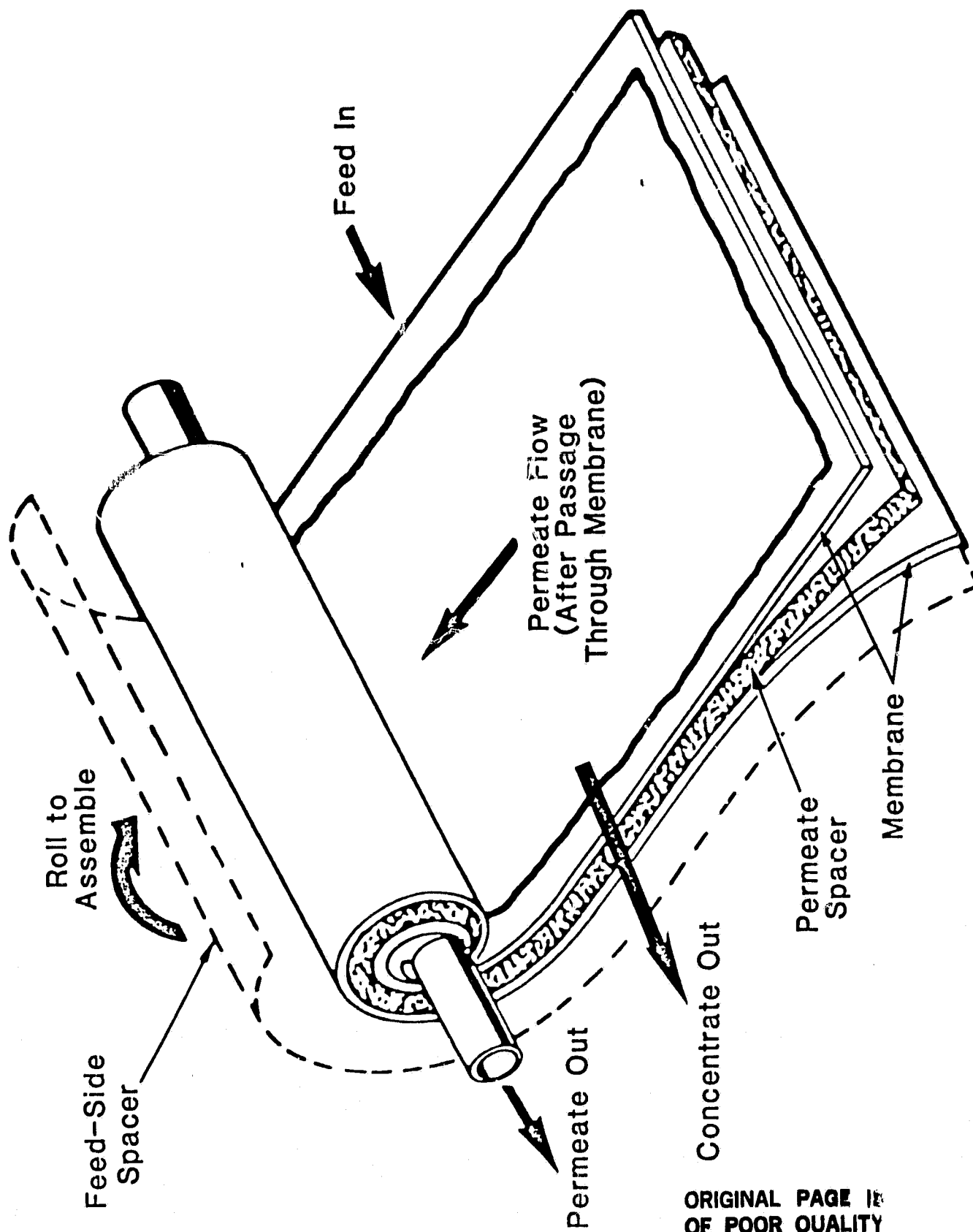


Figure 2. A single-leaf spiral-wound module. Photograph courtesy of Fluid Systems Division of UOP, Inc.

Concentration polarization and fouling are problems inherent to high-performance membranes. In membrane separations, part of the feed fluid permeates the membrane while the remainder is retained. The retained species exhibit a non-uniform concentration profile in the immediate vicinity of the membrane surface because of poor mixing of the feed fluid there. In processes such as RO, UF, MF, and gas separations, a "concentration polarization modulus" can be defined, expressing the ratio of the concentration of the retained species at the membrane surface,  $C_s$ , to that in the well-mixed bulk of the feed fluid,  $C_f$ . This modulus is given by

$$\frac{C_s}{C_f} = \exp\left(\frac{J\Delta x}{D}\right) ,$$

where  $J$  is the transmembrane flux of the permeating fluid,  $\Delta x$  is the boundary-layer thickness, and  $D$  is the diffusivity of the permeate in the fluid boundary layer. Modern, high-performance membranes generally exhibit high transmembrane fluxes and the polarization modulus can thus be severe unless the boundary-layer thickness is minimized; this is usually achieved by maintaining a high velocity of the feed fluid across the membrane surface, or by means of turbulence promoters. In gas separations, of course, the polarization modulus is minimal because the diffusivity of gases is so high. In UF and MF, however, and to a lesser extent in RO, the modulus is high because of the low diffusivity of the solutes that exist in the

solutions being processed. The formation of a gel layer similar to the cake formation common in ordinary filtration, is routine in UF, for example. Typically, therefore, UF equipment is engineered to operate in highly turbulent flow and high product recovery is achieved by operating in the feed-and-bleed mode.<sup>(10)</sup> Furthermore, provision for the use of clean-in-place chemicals is now routinely made in industrial UF plants. Reverse-osmosis plants similarly have pre- and post-treatment lines, and the plants are usually "tapered"<sup>(11)</sup> to maintain high feed-stream velocities even with high water recoveries. The MF industry is just now addressing many of these same issues, and the current solution is to operate in the cross-flow filtration mode.<sup>(12)</sup>

Also noteworthy is the fact that the RO industry has begun to install energy-recovery equipment in the larger RO plants. In RO, as in other pressure-driven membrane separation processes, the pressurized, concentrated reject stream carries with it a good deal of the process energy—in some cases more than 50%. Much of this energy can be recovered, either by means of a Pelton wheel or a recovery turbine.<sup>(13)</sup> Because of the capital costs involved, energy recovery only becomes economical today in plants of more than  $10^6$  gal/day capacity, but for those plants the energy requirements can be markedly reduced, as shown in the table below. Energy recovery is still somewhat experimental; in the near future, however, we can expect it to have a major impact on the energy requirements of pressure-driven membrane separation processes.



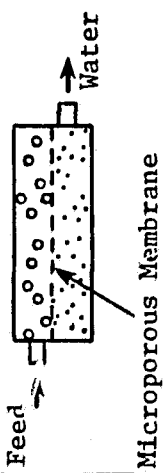
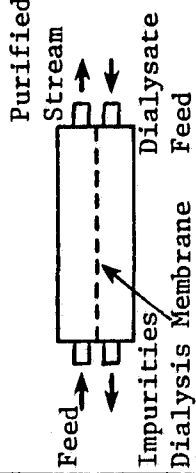
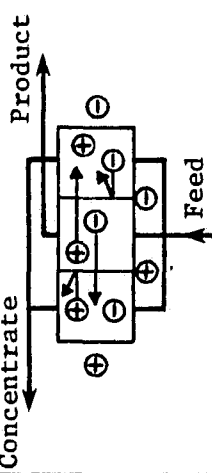
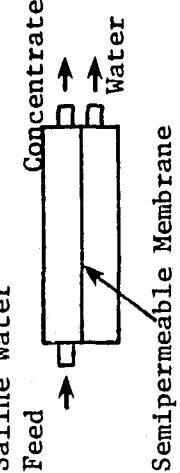
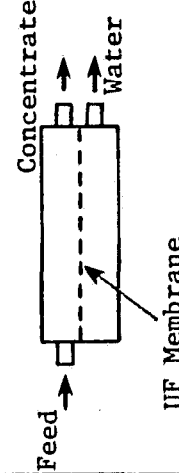
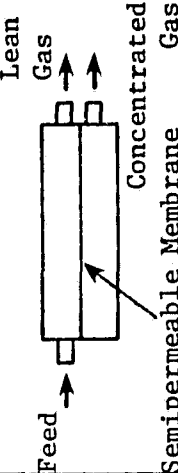
### Energy Consumption in Seawater Desalting Processes

	<u>kWh/m<sup>3</sup></u>
Multistage flash distillation	15.5
Vapor compression distillation	11
Reverse osmosis	9
Reverse osmosis with energy recovery	6.6

### B. APPLICATIONS

There are at present six defined membrane separation applications. A summary of these concepts, the materials passed and retained by the membrane in each, and the driving force is presented in the table on the next page. Several points are noteworthy.

- First, in all cases except MF, membrane processing takes a feed stream and divides it into two streams, one enriched in the product and the other depleted in the product. The separations are thus, in general, not complete or "clean," and one generally has to deal with two streams, the product and the reject stream. Membrane separations have been particularly successful where both streams have some value, as in some applications of UF and gas separations, or at least where the streams lacking in value do not have a substantial negative value. In fact, in the only existing applications of gas separations—"stream splitting" in such processes as hydrogenation or ammonia synthesis, and "acid gas" and natural gas recovery

PROCESS	CONCEPT	MATERIALS PASSED	DRIVING FORCE	MATERIAL RETAINED	APPLICATIONS
Micro-filtration		Water and Dissolved Species	Pressure Difference, Typically 10 psi	Suspended Material (Silica, Bacteria, etc.). Variable Particle-Size Cutoffs.	Sterile Filtration, Particle-Free Water Filtration.
Dialysis		Ions and Low-Molecular Weight Organics (Urea, etc.)	Concentration Difference	Dissolved and Suspended Material with Molecular Weight >1,000.	Blood Purification
Electro-dialysis		Ions	Voltage, Typically 1-2V/Cell Pair	All Non-ionic and Macro-molecular Species.	Water Desalination
Reverse Osmosis		Water	Pressure Difference, Typically 100-800 psi	Virtually All Suspended and Dissolved Material.	Water Desalination, Pollution Control, Food Concentration
Ultra-filtration		Water and Salts	Pressure Difference, Typically 10-100 psi	Biologicals, Colloids, and Macromolecules. Variable Molecular Weight Cutoffs.	Pollution Control and By-product Recovery, Especially Electrocoat Paint, Oil Emulsions, and Foods
Gas Separations		Gases and Vapors	Pressure Difference, 1-100 atm	Membrane-Impermeable Gases and Vapors.	Recovery of Hydrogen from Ammonia Synthesis, Refineries, Petro-chemical Plants; CO2 and Natural Gas Separation

in gas fields--both streams have a value and both are used at pressure. The success of the small but growing membrane gas separation industry is based completely on finding and exploiting such applications.

- In four of the six current applications, the fluid treated is water. In most of these cases, water is also the recovered product. There are a few exceptions. A narrow and specific application of ED occurs in Japan, where it is used to produce a concentrated brine from which salt is recovered by evaporation. Similarly, many UF applications would not be economical if some by-product were not recovered. However, in the other applications, water is the desired product. Water is the cheapest of all commodities, selling in many cases for only 20-30¢/ton, and it is reasonable to expect that if membranes can effect economic separations there, they can do so in other, less demanding applications.

- The only concentration-driven process is dialysis, and the only significant application of dialysis is in blood purification in people suffering from chronic or acute kidney disease, a process called hemodialysis. This is a life-saving or life-extending process in which cost is generally not a factor. There are only very limited industrial applications of dialysis because, put simply, concentration gradients produce low transmembrane fluxes and quite incomplete separations.

- Asymmetric or "skinned" membranes are used in all of these processes except dialysis, and concentration-polarization control is practiced in all of the processes except gas separation.

- Except in MF and UF, the membranes operate via a "solution-diffusion" mechanism. That is, the permeant dissolves in the membrane phase and diffuses across it, driven by a gradient in concentration, pressure, or electric potential. These membranes should thus not be viewed simply as very fine filters.

### C. SCIENCE

Membrane separations are based on differences in permeability, as we have already noted. The most useful fundamental studies of membrane permeation have focused on the two factors contributing to permeability: diffusivity and solubility. Our present understanding of both of these factors can be said to be correlative rather than predictive.

While it is obviously an oversimplification, our understanding of the fundamentals of membrane diffusivity are epitomized by the data in Figure 3. A general correlation exists between diffusivity in polymers and the molecular weight of the permeating species. The same correlation exists for diffusivity in liquids, which we know as the Stokes-Einstein relationship. However, in polymers there is an additional correlation that relates the slope of the  $\log(D)$ - $\log(MW)$  plot to the stiffness of the polymer backbone. For polymers with a low microviscosity, such as the room-temperature rubbers, the slope is

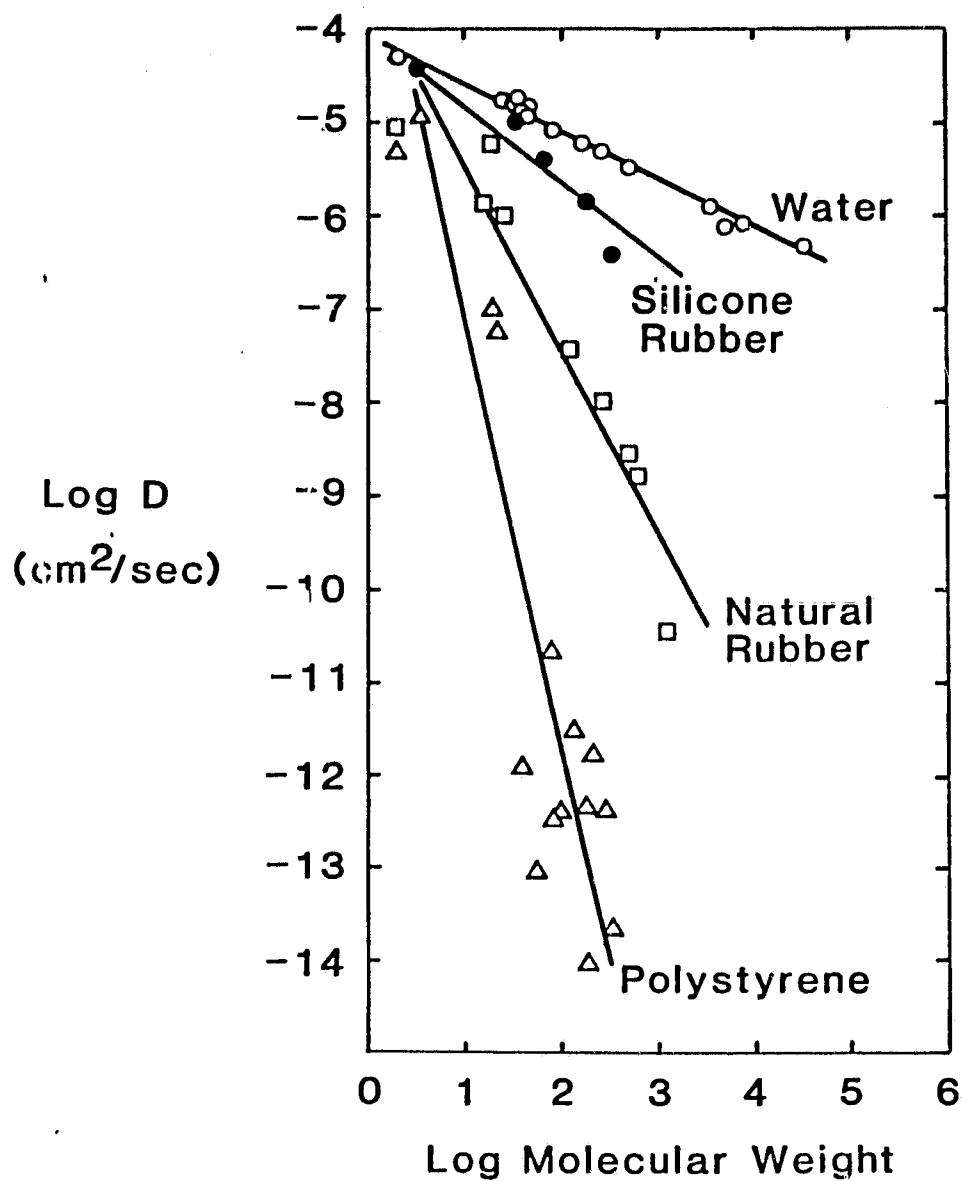


Figure 3. A log-log plot of diffusivity vs. molecular weight for a series of permeants in media of different viscosities. (14)  
The original data came from References 15-18.

in the range -2 to -3. (For water, it is  $-\frac{1}{2}$ .) For glassy or crystalline polymers, the slope is typically -5 to -6. Unfortunately, correlations of this type have not been studied in any detail, but we already have a grasp of the essential point: rubbery polymers have high diffusivities and therefore high permeabilities, in general. Unfortunately for membrane separations, diffusivities in rubbery polymers are only weakly dependent on molecular size; consequently, clean separations of chemically similar species cannot be effected by rubbery polymers. Glassy polymers, which include the so-called barrier polymers, do exhibit a large MW dependence of D, but diffusion coefficients generally tend to be so low that the high fluxes needed for efficient separations can only be achieved with very thin membranes.

Diffusivity is thus largely a function of the mechanical properties of the polymer. However, the chemistry of the polymer is also very important to permeability through its influence on the solubility of the diffusing species. Our fundamental understanding of solubility in polymers is still weak, and the best guidelines are still provided by the Hildebrand solubility correlations as embodied in solubility parameter diagrams. (19-21) While they are still essentially empirical, these diagrams do provide us with useful information. An example of a solubility parameter diagram, in this case for the polymer ethyl cellulose, is presented in Figure 4. (22) This diagram can be viewed as a kind of map: ethyl cellulose is soluble in (or at least

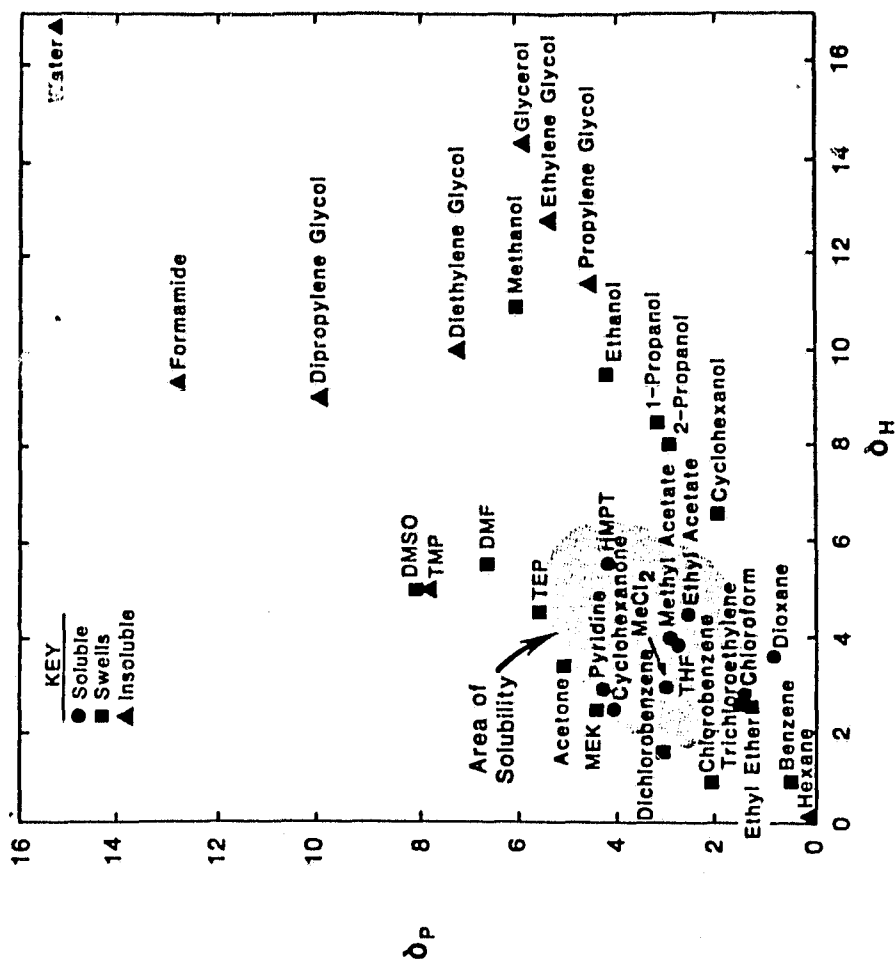


Figure 4. A solubility parameter diagram, showing the region of solubility of ethyl cellulose with a degree of substitution of 2.25. (22)

swollen by) those solvents in the shaded region of the diagram, and insoluble in all other solvents. Furthermore, the solvent solubility tends to decrease with increasing distance from the region of solubility. The polar and hydrogen-bonding elements of the solubility parameter,  $\delta_p$  and  $\delta_H$ , respectively, are now known for virtually all solvents and, by inference, for many crystalline solids, polymers, and even gases. The solubility parameter diagram of Figure 4 could be used, for example, to predict that ethyl cellulose should be highly permeable to dioxane but relatively impermeable to water, based on expected differences in solubilities. In principle, then, an ethyl cellulose membrane could be used to effect a separation between these two species and break the dioxane-water azeotrope.

The science of membrane separations is obviously more complex than these first-order D and S correlations suggest. The search for membranes to effect a desired separation has, in fact, been largely empirical over the years, and it is only quite recently that correlations of the type described here have come into use to provide guidance for membrane materials selection.

### III. CURRENT ACTIVITIES IN MEMBRANE TECHNOLOGY

A useful guide to the future of membrane technology can be derived by examining current trends of membrane R&D. These fall rather naturally into two classes: conventional approaches and unconventional approaches. The conventional approaches tend to be those undertaken in the less-well-



developed parts of the world, where the scientific establishments are attempting to catch up to Western technology. The most interesting work is that under way in the most advanced countries, i.e., in the United States, Western Europe, and Japan.

#### A. CONVENTIONAL APPROACHES

By "conventional approaches," we refer to those efforts aimed at incremental improvements or alternate but well-known approaches to existing technologies. We will not dwell on these, but merely cite some of them.

Work continues in the development of dialysis and electro-dialysis membranes, with particular emphasis on ED membranes made from inorganic ion-exchange materials. Hydrocarbon and other separations by pervaporation are also being studied. (Pervaporation is a process in which a membrane is interposed between a liquid mixture and a vapor stream, and the driving force for membrane permeation is the thermodynamic activity difference between the liquid and vapor phases.) Processes driven by temperature gradients—thermoosmosis and thermodialysis—are also being studied. The Loeb-Sourirajan technique for making effectively very thin membranes is still under study in some parts of the world.

We do not believe that these or other conventional approaches will lead to new applications of membrane technology. By and large, these areas have already been thoroughly researched in the most technologically advanced countries. Pervaporation<sup>(23)</sup> deserves special mention. It is a hybrid process, combining some of the features of membrane permeation

with those of distillation. Unfortunately, it also suffers from the principal drawback of distillation: high energy requirements. The heat of vaporization must still be supplied to the feed liquid, and the efficient recovery of this heat is not significantly easier in pervaporation than it is in distillation.<sup>(24)</sup>

## B. UNCONVENTIONAL APPROACHES

It is the areas cited in this section that we believe hold the most promise for the medium-range future (3-5 years) of membrane technology. This work can be grouped along these four lines: methods for making thinner membranes, in order to enhance flux rates; methods for increasing permselectivity; alternative engineering approaches; and nonseparation applications.

### 1. Thin Membranes

Far and away the most promising current approach to making very thin and imperfection-free membranes is the method of interfacial polymerization.<sup>(25)</sup> Several groups in the United States, including our own laboratory, and several in Japan are actively pursuing this approach. Ultrathin membranes are made by first impregnating a microporous substrate membrane with a solution of a reactive monomer or prepolymer and then contacting one surface with a second monomer in a solvent immiscible with the first solvent. With the proper choice of monomers, the polymerization reaction occurs very quickly, producing an interfacial film that is relatively impermeable to penetration by the monomers. The reaction is thus self-limiting and the

resulting film is extremely thin. Current activities in this area are centered on the development of high-performance, chlorine-resistant RO membranes, (26-27) and we believe there is some activity focused on gas separation membranes as well. The search for effective membranes is essentially empirical, because it is impossible to make a free-standing thick film of these interfacial polymers on which intrinsic permeability measurements could be made.

Two other approaches to preparing effectively thin membranes have also received some notoriety in recent years: these result in the "dynamically formed" (6) and "plasma polymerized" (7-8) membranes. After considerable research effort in several laboratories, neither of these approaches has led to the sort of reproducible membrane properties essential to technological development.

## 2. Improved Permselectivity

As we have already noted, the key limitation to membrane separations lies in the inability of conventional membranes to effect clean separations. It appears unlikely that new polymers will be developed that exhibit markedly improved permselectivity. Recent work in "coupled transport" and "facilitated transport" membranes shows great promise in alleviating this important limitation. These represent an entirely new approach to membrane separations. Selectivity derives from the incorporation of a specific carrier within the

membrane. Two sorts of carriers have been examined. In one, the carrier forms a complex with the target species on the feed side of the membrane, this complex diffuses across the membrane down its concentration gradient, and the target species is released on the product side of the membrane because the thermodynamic activity of the target species is lower there. This type of carrier-mediated transport process is referred to as facilitated transport. An important variation on this theme is referred to as coupled transport. In this process, as illustrated in Figure 5, the flow of the carrier complex in the forward direction across the membrane is coupled to the flow of the carrier in some other complexed form in the opposite direction. In the case illustrated in Figure 5, the carrier couples the flow of a univalent metal ion,  $M^+$ , from left to right with the flow of hydrogen ions from right to left. Typically, but not necessarily, the carrier is dissolved in a solvent that is held by capillarity within the pores of a microporous membrane.<sup>(28-30)</sup> In other variations, the carrier can be dissolved directly in a plasticized membrane, or the carrier may itself be the plasticizer,<sup>(31)</sup> or the liquid membrane containing the carrier may be free-standing in the form of a "bubble."<sup>(32)</sup> Regardless of how the carrier is contained, these membranes offer some substantial advantages over the conventional, solid, passive-transport membranes known heretofore:

With sufficiently specific carriers, virtually complete separations can be achieved. For example,  $Cu^{++}$  can be separated from  $Fe^{++}$  with separation factors exceeding  $10^3$ .<sup>(33)</sup>

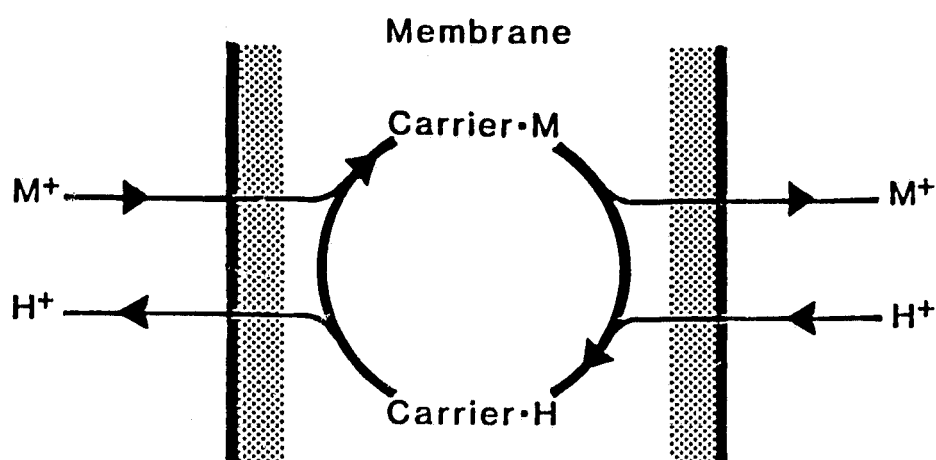


Figure 5. The mechanism of coupled transport.  $M^+$  denotes a monovalent metal ion.

b) Because diffusivities in liquids are generally orders of magnitude higher than diffusivities in solids, the permeation rates through liquid membranes are generally very much higher than can be achieved with conventional polymeric membranes.

c) In the case of coupled transport, the target species can actually be made to flow against its concentration gradient by imposing a gradient of the coupled species in the opposite direction. This is a result of the Donnan distribution law. For example, in our studies with coupled transport we have demonstrated "uphill" diffusion of copper, chromate, uranyl and other ions against concentration factors of  $10^4$  or more.

We believe that R&D in coupled and facilitated transport is now being conducted in more than a score of laboratories around the world.

### 3. Alternative Engineering Approaches

Thus far, we have focused entirely on current R&D aimed at improving membrane performance. However, membrane separations can also be made more effective or more efficient by other means. Two examples will illustrate this point. Hwang<sup>(34)</sup> has recently proposed a continuous membrane column for the separation of gaseous mixtures. While not entirely new,<sup>(35)</sup> this is an ingenious way of improving the separation efficiency of membranes without any alteration in the membrane properties. A sketch of the continuous column is presented in Figure 6. The feed gas mixture enters the system under pressure between the two membrane separation units, as shown.

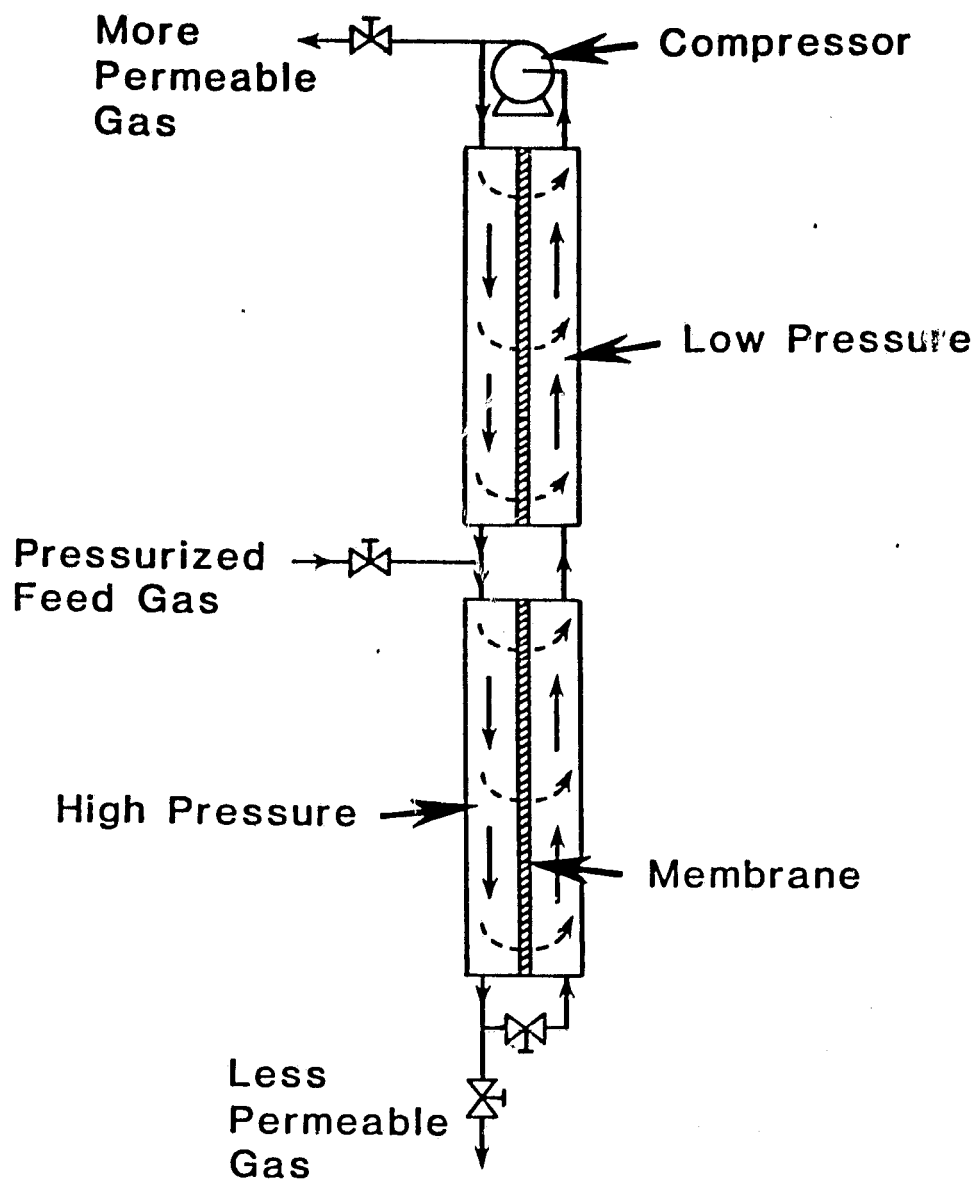


Figure 6. Hwang's continuous membrane column. (34)

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As the feed stream moves downward, some of the more permeable gas permeates the membrane, leaving the feed stream enriched in the less permeable gas. If the lower membrane unit is made increasingly long, an increasingly pure stream of the less permeable gas is left, and a fraction of this is removed at the bottom of the column. The remainder of the gas stream is then shifted over to the low-pressure side of the membrane column where, as it rises up the column, it becomes increasingly enriched in the more permeable gas. A fraction of this gas stream is then removed at the top of the column. The remaining gas mixture is then recompressed and fed back into the top of the column.

This continuous column has some of the properties of an infinite membrane cascade, but it does not require intrastage compression as conventional cascades do.<sup>(36)</sup> By reducing the fractional recovery of the gases, the purity of the two gas streams can be increased, in principle, without limit. Hwang has already demonstrated, for example, that silicone rubber membranes operated according to this column principle can be used to produce up to 60% O<sub>2</sub> using air as the feed stream. In a conventional single-stage membrane separator, the maximum O<sub>2</sub> purity that can be achieved is only 35%, even at negligible O<sub>2</sub> recovery, because of the low permselectivity ( $\alpha_{O_2/N_2} = 2$ ) of silicone rubber. In a sense, then, this column allows one to trade off increased energy of recompression with increased product purity. In some instances, this may well be an energy-efficient trade-off, as Hwang has shown.<sup>(37)</sup>



Several laboratories are involved in exploiting this development. At Bend Research, for example, we are looking at applications involving liquid separations, such as the separation of ethanol from water.

Another alternative engineering approach is based on the idea of changing the nature of the target species in the feed solution so as to render the membranes more or less permeable to it. There have been several manifestations of this idea already reported. In reverse osmosis, the rejection of certain species, both neutral<sup>(38)</sup> and charged,<sup>(39)</sup> has been markedly improved by forming stable complexes. The RO membrane is substantially less permeable to these higher-MW complexes than to the target species. The same idea has been applied in UF, particularly for the removal from solution of toxic heavy metal ions.<sup>(40)</sup> In that study, strong complexing agents were used to tie up the heavy-metal ions in solution. The solution was then ultrafiltered, the metal complex broken, and the complexing agent recovered for reuse. Still another application of this idea has been proposed for the separation of proteins.<sup>(41)</sup> Macromolecular, protein-specific binding agents were used to create macrocomplexes that were retained by UF membranes that passed the uncomplexed protein. Trypsin and chymotrypsin, with nearly identical molecular weights, were separated in this way.

#### 4. Nonseparation Applications

While the thrust of this report has to do with membrane separations, there have been developments in recent years, which could have significant impact on energy utilization, in which the membrane is not used primarily to effect a separation. We will cite two such areas that we believe have promise.

##### a. Biotechnology

This subject, of course, is one of the most important new technical areas in the world today. Membrane processes could well play an important role in the utilization of biotechnology. Two examples of potential applications have recently been reported. One involves a membrane reactor consisting of a two-layer membrane laminate.<sup>(42)</sup> One layer contains an immobilized, water-immiscible solvent, specific for the substrate; the other layer contains an enzyme (or other catalyst). Substrate from an aqueous feed solution enters the first membrane layer, is converted to product by the enzyme in the second membrane layer, and the product then permeates the second layer into an aqueous product stream. This laminated-membrane reactor combines selective reaction with separation. Suggested applications include the production of chemical intermediates and specialty chemicals.

A second type of membrane bioreactor has also been described.<sup>(43-44)</sup> In this approach, a porous hollow-fiber membrane is used to immobilize enzymes, either in the free state or within cells. The substrate flowing down the fiber lumen freely permeates the fiber wall, where it is converted into

product. The product then diffuses back into the flowing stream in the fiber lumen. With a sufficiently long flow path, essentially complete conversion of substrate to product could be effected.

Both of these examples should be considered to be only first-order attempts at using membrane technology to aid biochemical conversions and separations. In neither example is there clear-cut synergism. That is, there is not an overwhelming case for combining the enzymatic reaction within the membrane separation step, as opposed to carrying out the process sequentially, i.e., enzymatic conversion followed by membrane separation.

b. Energy from Sunlight

The direct conversion of sunlight into electrical energy is, of course, the subject of considerable R&D around the world today. Most of that work is based on inorganic systems.

Light-induced redox reactions are also known to occur across membranes. The best-known example is photosynthesis, the primary events of which occur across a thin membrane referred to as the thylakoid vesicle within certain plant cells. Those photochemical reactions are mediated by chlorophyll. Much of the research in this area is being done by biophysicists in an attempt to understand photosynthesis. (45)

There is now a limited amount of research under way in the area of photosynthesis analogs, i.e., light-induced redox reactions occurring across synthetic membranes. A quinone-type

carrier, vitamin K<sub>3</sub>, has been incorporated into a liquid membrane to produce a light-induced redox system.<sup>(46)</sup> Electron transport across membranes in the form of phospholipid liposomes containing chlorophyll has been reported.<sup>(47)</sup> Photo-induced potentials of greater than 100 mv have been reported for chlorophyll-containing lipid bilayer membranes.<sup>(48)</sup> Redox reactions have also been achieved across synthetic polymeric membranes containing vitamin K<sub>1</sub> as the electron carrier.<sup>(49)</sup>

This work is all primitive vis-à-vis its energy conversion implications. It is clearly too early to say if any of these directions could lead to practical systems for harnessing sunlight.

#### IV. FUTURE DIRECTIONS

In the early days of the "energy crisis," there was an inordinate amount of activity in this country directed toward alternate forms of energy, such as wind, solar, tidal, wave, ocean-thermal gradients, salinity gradients, and so on. While work is still going on in several of these areas, it is clear that most of these forms of "free" energy are not only far from free, they are not even competitive as energy sources with \$35/bbl OPEC oil. We would hope that that experience has taught us that energy-converting or energy-saving schemes should be subjected to rigorous economic feasibility studies before the more expensive research, development, engineering, and pilot-plant projects are undertaken. Membrane processes, and especially membrane separations, have

experienced a spectacular growth in recent years. Still, they are not ideally suited to all separation applications. nor are they inherently simpler or cheaper than conventional separation processes. In this final section, we will cite those areas where we believe government or private R&D support for membrane processes is most likely to yield a positive return.

#### A. WHERE TO LOOK

It is our conviction that the earliest and surest returns will be found by attempting to exploit existing technology. The breakthroughs in membrane technology in recent years have come about so quickly that technicians in related fields have not yet had time to digest them.

A good case in point is the recently introduced Monsanto PRISM<sup>TM</sup> membrane-based system for separating gases.<sup>(50)</sup> The Monsanto group made two types of breakthroughs. The first was technical: they produced skinned, highly permselective, hollow-fiber membranes; and they found a way to avoid leaks, which are especially detrimental to gas separations.<sup>(51)</sup> The second sort of breakthrough was not so obvious, but was equally important in our opinion: they identified industrially important and economically feasible applications for the new separation technology. An example is the partial separation of  $H_2$  from  $CH_4$  in refinery streams, where the feed stream is already at pressure and both the permeate and raffinate

streams from the membrane permeator have a value. Identifying these viable applications has led to a new industry of rapidly growing importance.

It is this identification of feasible applications—as opposed to force-fitting membrane processes into important but technically unlikely applications—that we believe will have the greatest payoff. The technology at our disposal was cited in sections II and III: methods of making and modularizing extremely thin, leak-free membranes; coupled- and facilitated-transport membranes that exhibit high fluxes, high permselectivities, and, in some cases, "uphill" diffusion; and the Hwang continuous column principle. Some of the areas where these elements can be utilized include:

- The separation of the acid gases, and particularly  $\text{CO}_2$ , from natural gas streams to upgrade the gas stream and to recover the  $\text{CO}_2$  for use in secondary oil recovery. A small amount of work is already in progress in this area.

- The recovery of oxygen and nitrogen from air with facilitated-transport membranes. Oxygen-enriched air can be used in synfuels production and nitrogen can be used for "blanketing" and other industrial applications. Our laboratory has already had some success in this area.<sup>(52)</sup>

- The separation of ethanol or other potential substitute liquid fuels from the liquors produced in fermentation tanks using grain or biomass sources. The Solar Energy Research Institute has initiated a small effort in this area.<sup>(53)</sup> The CSIRO in Australia has recently undertaken a promising study for the recovery of volatile

fatty acids from a biomass converter using a coupled-transport membrane process. (54)

- The recovery of heat from industrial drying processes. Most of that heat is present in the water vapor, and it could be recovered by passing the vapor through an air-impermeable membrane. (55)

- The recovery of metals from the hydrometallurgical leach solutions now prevalent in the mining industry by coupled-transport membranes.

- The concentration and separation of acids, bases, and salts in solution by a form of ion exchange known as Donnan dialysis. (56)

- The generation of acids and bases by means of so-called bipolar membranes. (57)

- Chemical or biochemical conversions in which immobilized catalysts are combined with membrane separators.

- The direct production of energy from sunlight by means of membranes containing chlorophyll analogs.

## B. HOW TO LOOK

It is now possible to estimate the costs of membrane separation processes based on the body of practical data already established in such fields as reverse osmosis. Modularized membranes now sell for \$1-10/ft<sup>2</sup> of membrane area, depending on the application, and the membrane modules typically represent one-third of the capital cost of a membrane separation plant. The costs of energy, labor, and chemicals are generally

easy to estimate. We believe that any new process should first be subjected to a careful economic analysis, based on data such as these.

The risks in a technology-first, economics-second approach are substantial. The Standard Oil Co. of Indiana spent a good deal of time and money in an attempt to develop a membrane-based process for the separation of olefins from paraffins using silver-based complexing agents specific for olefins. About ten patents were issued to the Standard Oil scientists in this area.<sup>(58)</sup> In spite of favorable technical performance, the project was recently dropped because of unfavorable economics.

Membranes are especially suited to achieve partial separations. The possibility of reducing energy requirements and overall costs by combining a first-stage membrane process with a second-stage cryogenic, distillation, absorption, or other type of process should be examined. The important area of petrochemical separations, or those involved in the production of large-volume chemicals, could well be subjected to an economic feasibility study now. Such studies are beyond the scope of this report, but the methodology to be used and the cost factors and projected membrane performance are already available to those skilled in the art. They would require cooperation by those in both the private and public sectors who are knowledgeable in the economics of existing technologies and who are in a position to prioritize national needs.



An important adjunct to technological and economic factors is the state of membrane transport fundamentals. Our knowledge of membrane permeability and permselectivity is still superficial, and a joint, long-range DOE-NSF program in membrane transport fundamentals would likely bear fruit. Particular attention should be paid to the new high-performance coupled- and facilitated-transport membranes, and suitable carriers should be sought from among the voluminous literature of inorganic and biological chelation or other type of complexing agents.

Finally, any program aimed at exploiting membrane technology should remain responsive to future breakthroughs. The worldwide activity in membranes is now so broad-ranging and intense that unplanned advances that will alter current thinking and economics seem a virtual certainty over the next several years.

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